

## CONCEPT DISCUSSION

The approach to solving the pollution problem has consisted of two parts. First an attempt has been made to eliminate several of the pollutants from the effluent stream, both by process modifications and waste treatment. By modifying the kiln firing procedure, it was hoped that Hf could be eliminated from the 2nd stage of the process. Also, by pH adjustment, silica could be removed as a gel.

Since it has been found that Hf cannot in fact be eliminated, and that this approach could not remove CaCl<sub>2</sub> from the effluent, a second approach has become necessary. This approach has been to minimize liquid volumes employed in the process, and to recycle all effluent streams so that only solid effluent leaves the plant.

The most significant characteristics of the recycle system which is being proposed as a result of this study include:

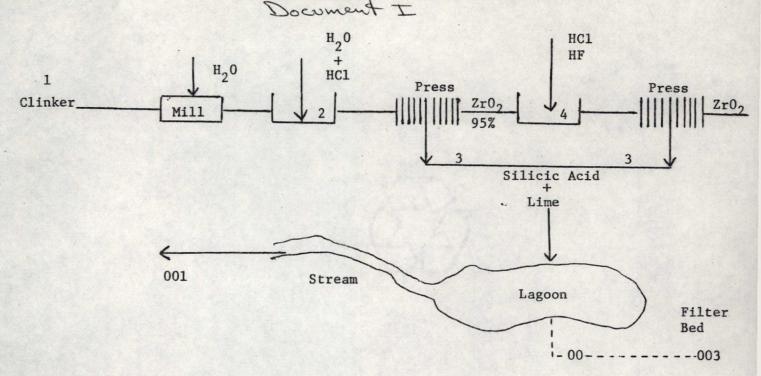
- lst stage effluent is treated to remove silica gel, which also entrains some water and CaCl<sub>2</sub>. The treated filtrate, which contains CaCl<sub>2</sub>, is then recycled to the lst stage, along with recycled 2nd and 3rd stage water. ("3rd stage" refers to the final product water wash stage.)
- 2. Part of the 2nd stage untreated effluent is recycled to the second stage, along with recycled 3rd stage water, and fresh HCl and Hf. The rest of the 2nd stage effluent is treated to remove fluoride as  $CaF_2$ , and silica gel as done in the 1st stage of the process. The treated filtrate which contains some  $CaCl_2$  and traces of  $CaF_2$ , is then recycled to the 1st stage.
- 3. 3rd stage filtrate, water which is still low in impurities, is recycled to the 1st and 2nd stages, and also to the  $Ca(OH)_2$  slurry tank.

Advantages of the proposed system over the existing system include:

- 1. Liquid effluent eliminated.
- 2. Water usage decreased by more than 1/2.

- 3. HCl usage decreased by up to 20%.
- 4. More efficient water utilization as a result of countercurrent usage scheme.
- 5. Proposed system could eventually be operated continuously, with some modification.

## PRESENT ZIRCOA GRAIN PLANT PROCESS



Chemical Engineering has been asked to do a study of Zircoa's pollution problem, which consists of the following pollutants in the plant liquid effluent:

POLLUTANT	1974 LEVEL
Chloride	5,000 ppm
Fluoride	5-25 ppm
Silica ) Dissolved	9-14,000 ppm
Calcium Solids	

These pollutants are introduced into the system as four species.

1. SILICA, and part of the CALCIUM, are introduced in the feed to the process:

$$CaCO_3 + ZrSiO_4 --- > ZrO_2 \cdot CaSiO_3 + CO_2$$

2. CHLORIDE is introduced as HCl, used primarily in the 1st stage extraction of material from the kiln:

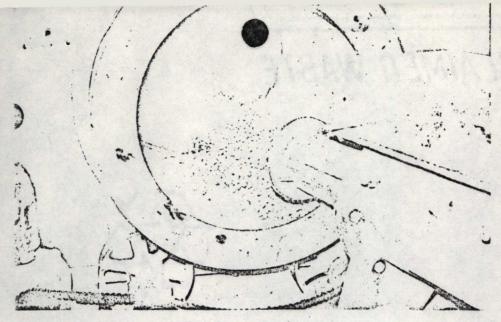
$$Zr0_2 \cdot CaSi0_3 + 2HC1 \longrightarrow Si0_2 \cdot H_20 + Zr0_2 + CaCl_2$$

3. The remaining CALCIUM is introduced as Ca(OH)<sub>2</sub> used for neutralization of the acid effluent streams:

$$Ca(OH)_2 + 2HC1 \longrightarrow CaCl_2 + 2H_2O$$

4. FLUORIDE is introduced as HF, used in the 2nd stage extraction to remove residual silica, calcium:

$$6HF + Zr0_2 \cdot C1^- \cdot Si0_2 \cdot H_20 \longrightarrow H_2SiF_6 + 3H_20 + C1^- + Zr0_2$$



Extruded slugs are rounded in this rotating drum.

feeders meters small batches of calcine to the ball mill at one minute intervals. Batches are weighed to an accuracy of  $\pm 0.1\%$ .

Undersize material (-200 mesh) is pumped to one of three 2500 gallon reaction tanks agitated by Lightnin' mixers. Clinker slurry is leached with a hydrochloric acid solution in the reaction tanks to dissolve the soluble calcium silicate formed in the rotary kiln. The leaching action is instantaneous, occurring as soon as contact is made in the reaction tank.

In production, three tanks are leached and fed to one of five Sperry er presses for separation of the zirconium oxide. Two filter press loads are leached a second time and filter pressed again to make up a batch. The batch is neutralized in the filter press and dried at 1000-1200 F in a gas fired drier. A 10,000 pound rotary blender combines batches to provide lot number designations for raw material quality control purposes. Filtrate is neutralized with lime and pumped to a settling pond adjacent to the plant.

## **Grog Production**

For some applications the zirconium oxide produced by the leaching process must be fired to 3250 F to produce high-fired zirconium oxide grog. To produce the required grog, zirconium oxide is extruded and cut into brick-like shapes called dobies and fired in pot furnaces to the desired temperature.

Fired dobies are crushed and screened to particle size specification. A recently installed grog sizing system consists of a Pennsylvania Crusher vertical impact pulverizer fed by a Syntron vibratory feeder and serviced by a Sly dust collector. The pulverizer reduces grog particle size by impacting

